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Comparative study between a CMS membrane and a CMS adsorbent: Part II. Water vapor adsorption and surface chemistry

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ABSTRACT

The adsorption/desorption equilibria of water vapor in a carbon molecular sieve (CMS) membrane and a commercial CMS adsorbent were determined, exhibiting S-shaped, type V isotherms. The fits of several models found in the literature to the experimental data were evaluated. The results obtained led to the development of a new model accounting for both adsorption and desorption and essentially based on the work of Lagorsse et al. (2005) [15]. Furthermore, the adsorption kinetics was also assessed for both materials and well described by a linear driving force model. The existence of hydrophilic groups responsible for water vapor adsorption in such carbonaceous materials has been related to the surface chemistry by means of X-ray microanalysis and by thermogravimetry. It was concluded from X-ray microanalyses that the carbon membrane presents a lower C/O ratio and is thus more sensitive towards water vapor exposure, as evidenced by the measured water adsorption at lower relative pressures. It was also observed that the diffusion rates are higher for the CMS membrane than for the CMS adsorbent.

1. Introduction

The present paper continues the comparative study between a carbon molecular sieve (CMS) membrane and a commercial CMS adsorbent suited for gas separation, reported in the part I of this work, giving now emphasis to the surface chemistry of these materials.

It is widely known that many gaseous streams present water vapor to some extent [1]. In the particular case of the separation of nitrogen and oxygen from air using carbon molecular sieve materials, the influence of water vapor is of significant interest [2]. The presence of a small amount of water can sometimes disable or decrease the performance of the adsorbents [3].

These materials are mainly constituted of carbon atoms distributed as disordered graphene layers that work as hydrophobic sites for adsorption. However, some heteroatoms are also present, conferring a hydrophilic character to these carbon structures and allowing for the adsorption of water [4–6]. The heteroatom more often present in these structures is oxygen, which can assume different forms, as hydroxyl, carboxyl, quinine, peroxide or aldehyde functional groups [1,3,7]. Water molecules establish hydrogen bridges with the oxygen on the surface, known as primary adsorption sites [4,8], and subsequent water molecules will then bond to the previously adsorbed water molecules [8]. When this molecular cluster becomes sufficiently large, dispersion forces become predominant and it leaves the primary site adsorbing thereafter into hydrophobic micropores [9]. The adsorption isotherm is therefore a function of the concentration and distribution of primary adsorption centers, pore structure and vapor pressure [3,10].

According to IUPAC designation, the adsorption of water vapor in carbon materials having oxygen functional groups exhibits a type V isotherm also known as S-shape [9,11–14]. It has been discussed in literature that hysteresis in such materials may be explained by differences between filling and emptying mechanisms, rather than by condensation in mesopores [8,15].

In the part I of this paper a carbon molecular sieve adsorbent from Takeda (MSC3K-162) and a carbon molecular sieve hollow fiber from Carbon Membranes, Inc. were studied. Their structural properties were compared and their influence on the performance of each material was assessed through several characterization techniques (scanning electron microscopy, X-ray diffraction, mercury porosimetry, micropore size distribution). The determination of equilibrium isotherms and kinetic parameters for N_2, Ar, CO_2 and O_2 was performed at 29.5 °C. In this second part, both materials are characterized by thermogravimetric analyses, assessing the fixed carbon content and the volatile matter related to heteroatoms existent on the surface. The surface chemistry of each material is investigated by X-ray microanalysis and related to water vapor adsorption/desorption equilibrium and kinetics. The way how the different heat treatments influence the final hydrophilic group content [16] was also analyzed. The adsorption of water vapor on these groups provides meaningful information about the structure of the

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carbonaceous materials. The experimental adsorption curves were fit by models described in the literature and a new model is also proposed.

2. Experimental

2.1. Materials studied

The carbon molecular sieve membranes designated here as HF CM were provided by Carbon Membranes Ltd., an Israeli company that bankrupted meanwhile. MSC3K-162 is a commercial carbon molecular sieve adsorbent supplied by Takeda and indicated for nitrogen production from air by PSA.

2.2. Thermogravimetric analysis (TGA)

The materials under study were submitted to a proximate analysis by thermogravimetry in order to determine their content in moisture, volatile matter, fixed carbon and ashes. The analyses were performed in a Netzsch TG 209 F1 Iris thermogravimetric balance, with 10^{-5} g precision; samples of 5 mg were used. The feed gases were N_2, up to the oxidation stage (950 °C), and O_2, afterwards. The temperature protocol used was mainly based on the work published by Ottaway [17] and is presented in Fig. 1. The heating rate was 25 °C min^{-1}, with dwells at 50 °C, 110 °C and 950 °C. The long dwells used at 50 °C and 110 °C are mainly related to O_2 removal for preventing oxidation at higher temperatures. The dwell at 110 °C assures that all water is removed. The final dwell at 950 °C has a total extent of 20 min, divided in two subdwells; 9 min under N_2 for volatile matter release and 11 min under oxygen for assessing the ash content.

2.3. X-ray microanalysis

The surface chemistry of both MSC3K-162 and HF CM was assessed by X-ray microanalysis using a FEI Quanta 400FEG/EDAX Genesis X4M. These analyses were performed in simultaneous with SEM, already presented in the part I.

2.4. Adsorption

The sorption studies in the CMS membrane and adsorbent were conducted using the gravimetric method, in the same magnetic suspension balance from Rubotherm® (metal version and 10^{-5} g precision) already presented in the part I of this publication. However, the system has been adapted to allow sorption studies towards water vapor, as illustrated below: a small tank filled with liquid water was added for supplying vapor, up to the desired pressure, to the 5 L feeding tank; this system is represented in dashed lines in Fig. 2. The samples were regenerated with helium at 70 °C before and after water vapor measurements. Nitrogen was used to check the adsorption stability of the materials by determining adsorption equilibrium values and uptake curves before and after vapor exposure.

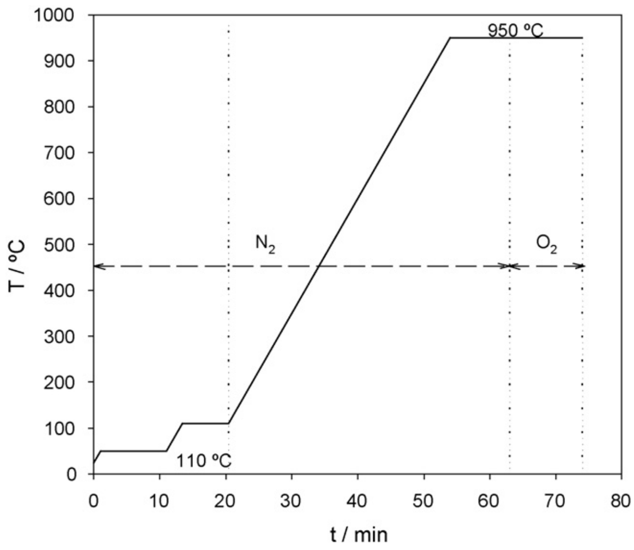

Fig. 1. Procedure for proximate analysis.

3. Results

3.1. Thermogravimetric analysis

Proximate analysis by thermogravimetry has been performed for MSC3K-162 and HF CM. The mass fraction of the sample is represented in Fig. 3, employing the heating protocol described

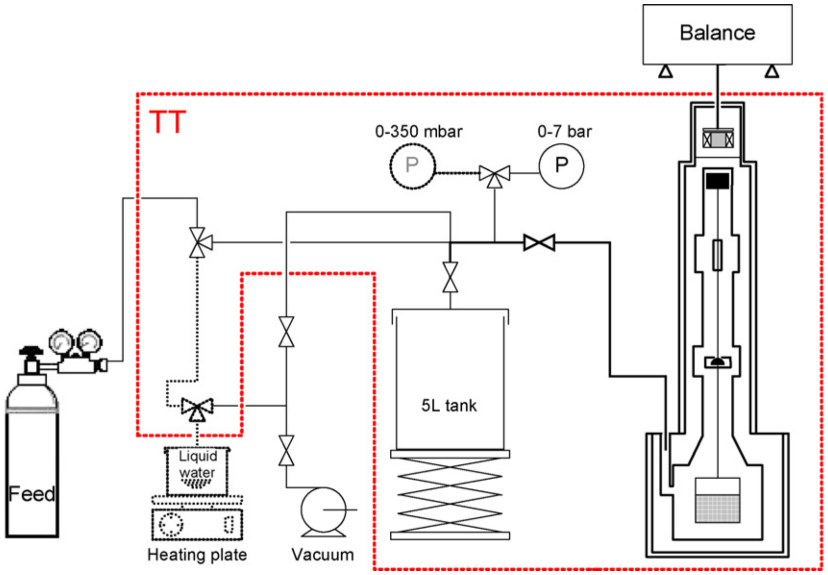

Fig. 2. Schematic representation of the gravimetric apparatus adapted for water vapor studies (adapted from [18]).